Synthesis of Metal Nanoparticle-Decorated Carbon Nanotubes under Ambient Conditions

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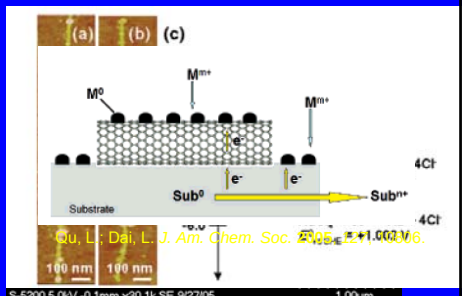
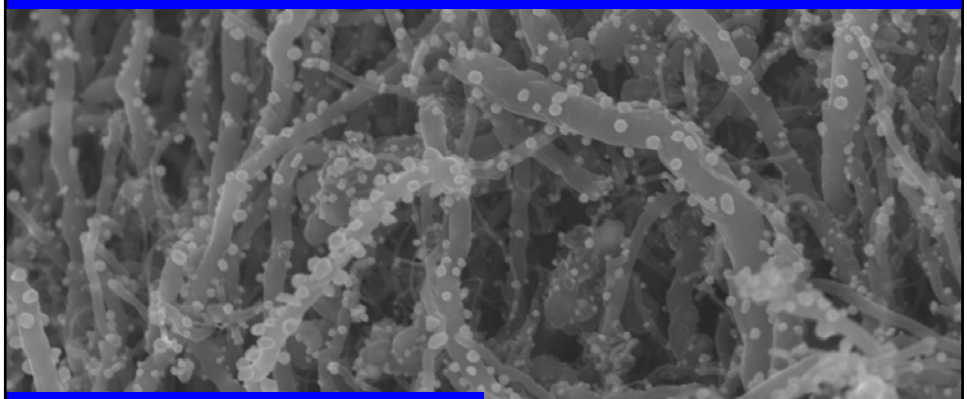
Preparation of Metal Nanoparticle-Decorated CNTs

- Metal nanoparticles + CNT
- Electrochemical methods
- Electroless methods
  - Sputtering
  - Activation bath
  - Use of reducing agents
    - Solid-phase reduction
      - H_2
    - Dispersion in solvents
      - $NaBH_4$
      - Ethylene Glycol
  - Pyrolysis from organometallic compounds
  - Spontaneous reduction
  - Substrate-Enhanced Electroless Deposition (SEED)



Choi, et al., *J. Am. Chem. Soc.* **2002**, *124*, 9058.

Thermal Decomposition of Metal Acetates in the Presence of CNTs



- Electroless
- Solventless
- No added reducing agent
- Readily scaled-up

$$CH_3COOAg \xrightarrow[\Delta]{CNT} Ag + CH_3COOH + C + CO_2$$

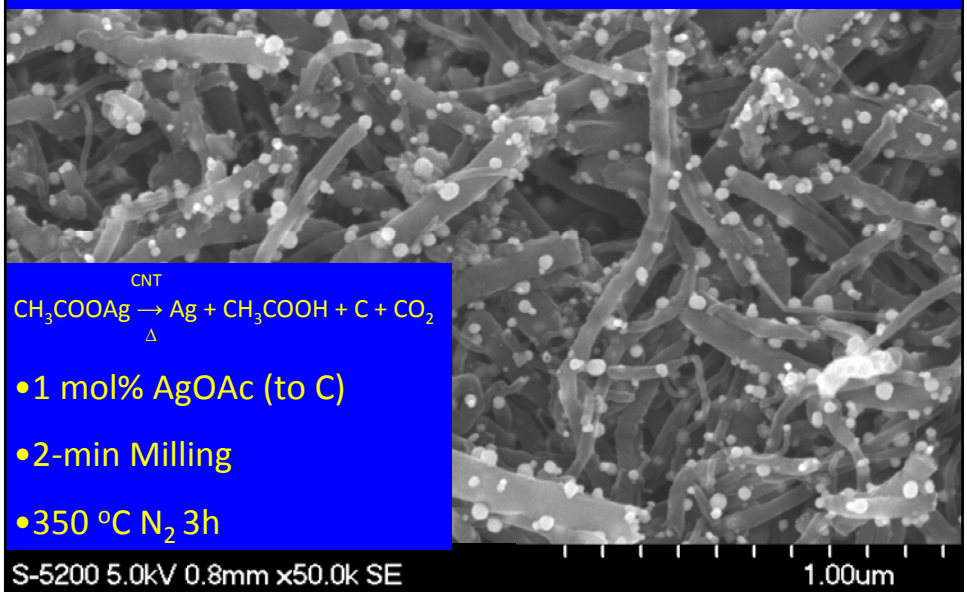
Patent Pending

1.00um

To Improve from Mortar/Pestle Mixing

- SPEX CertiPrep 8000D ***High-Energy Shaker Mill***
  - ~1000 cycles/min
  - 2.25" back and forth and 1" side-to-side movements
  - Zirconia vial: ~20 mL mixing load
  - Two zirconia balls: d ~ 0.5"

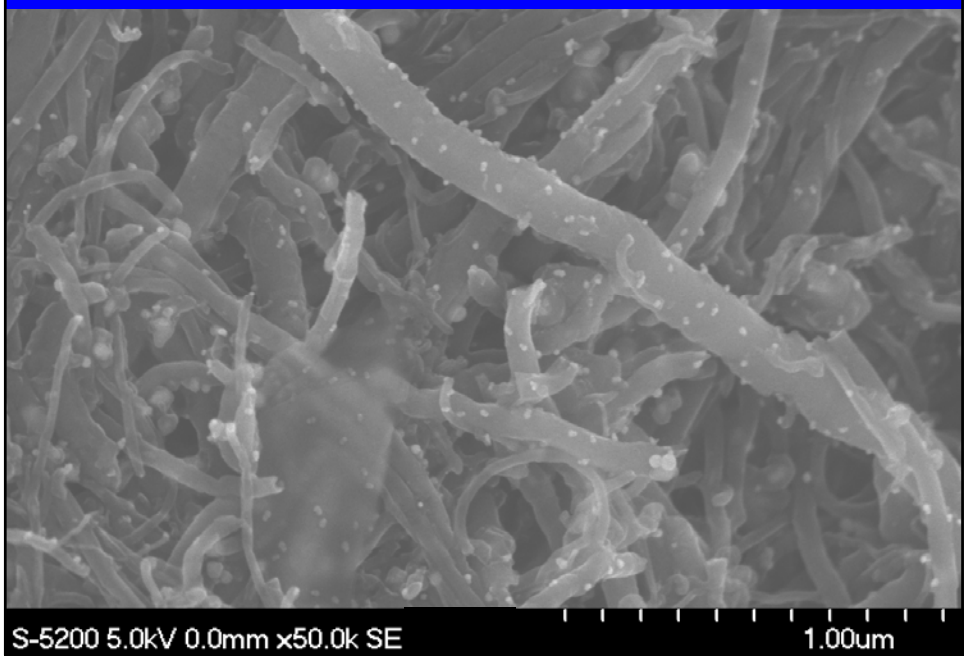
Thermal Decomposition of Metal Acetates in the Presence of CNTs



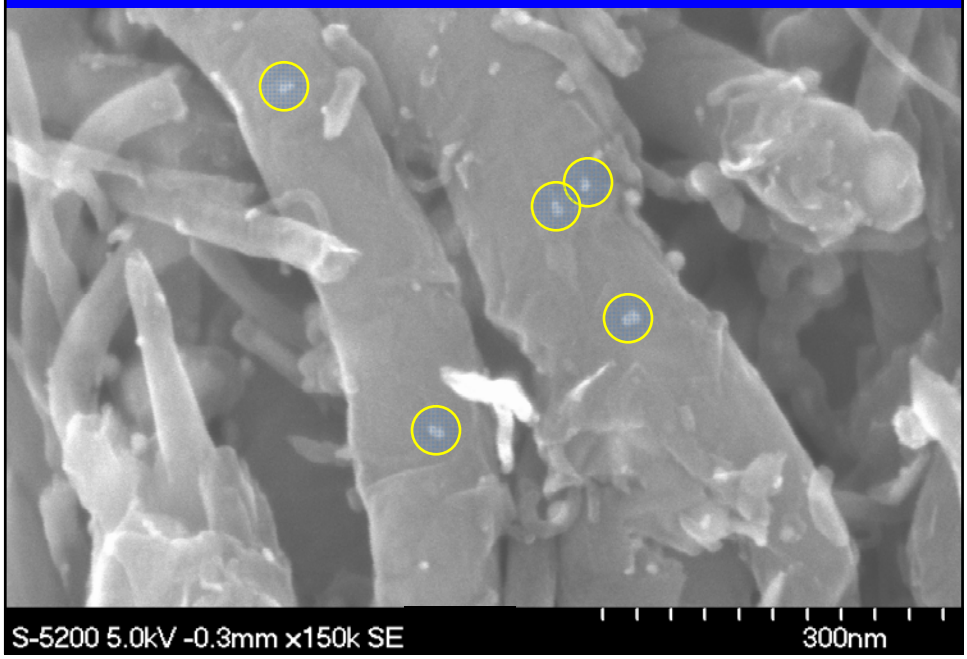
$$CH_3COOAg \xrightarrow[\Delta]{CNT} Ag + CH_3COOH + C + CO_2$$

- 1 mol% AgOAc (to C)
- 2-min Milling
- 350 °C N_2 3h

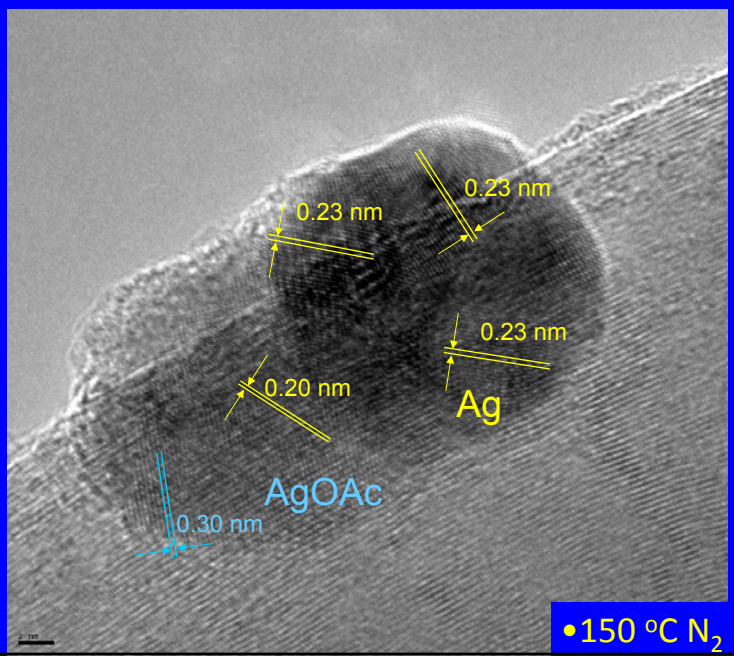
2-min Milling *without* Thermal Treatment



Sintering or Intermediate?

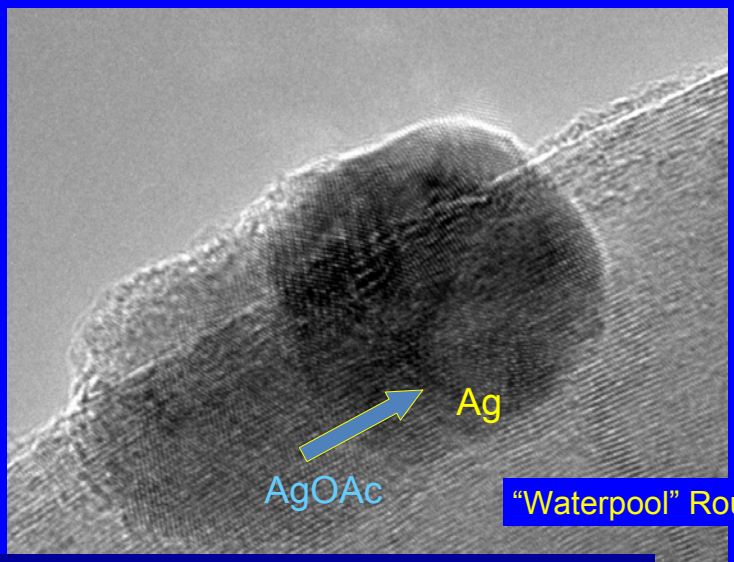


Sintering or Intermediate?



- 150 °C N_2

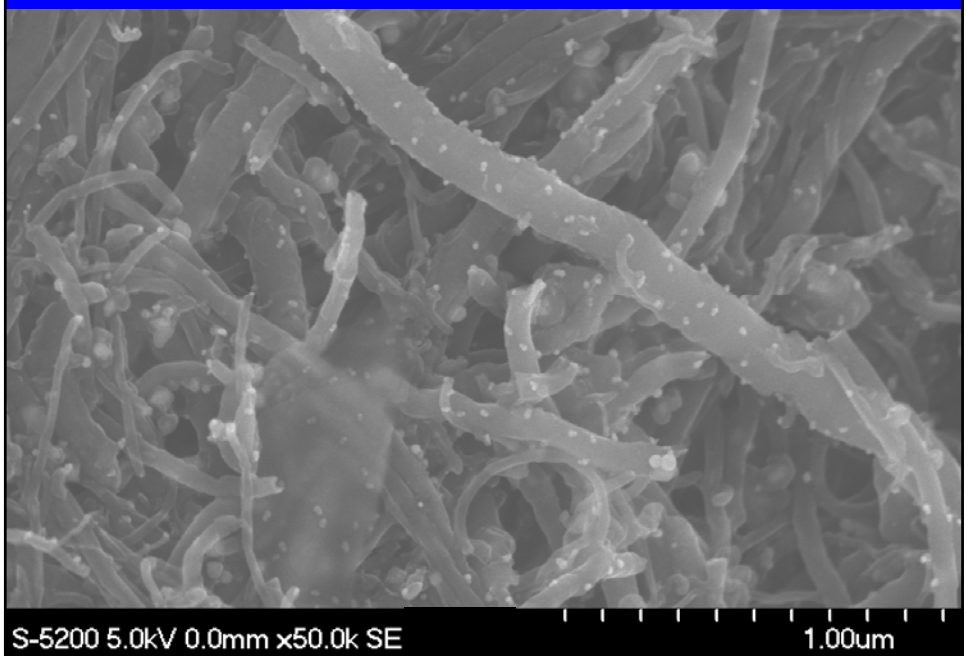
Sintering or Intermediate?



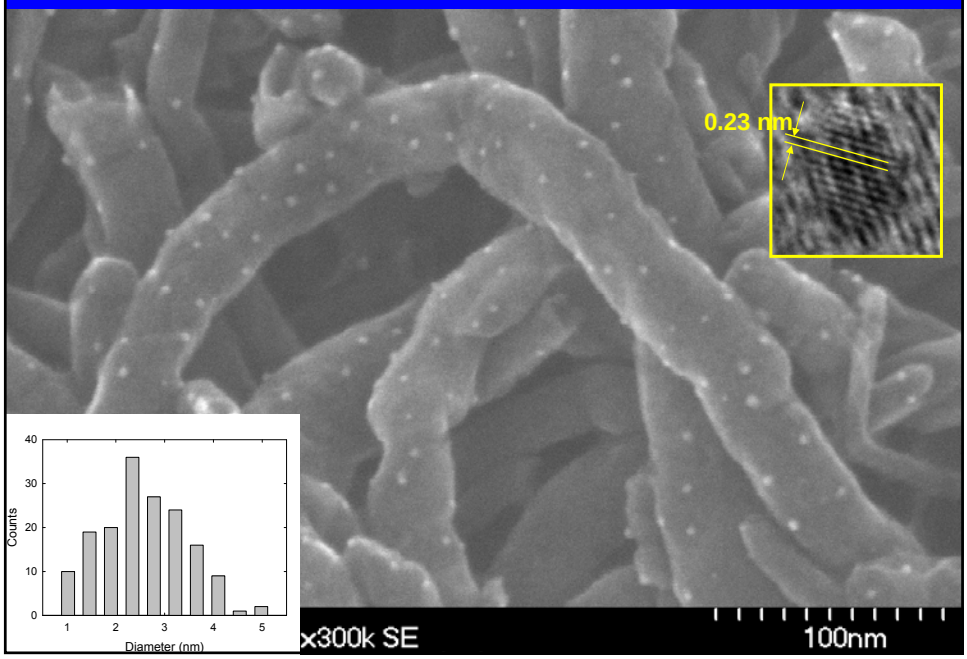
"Waterpool" Route

1. Formation of AgOAc nanoparticles
2. Decomposition of AgOAc on C surface

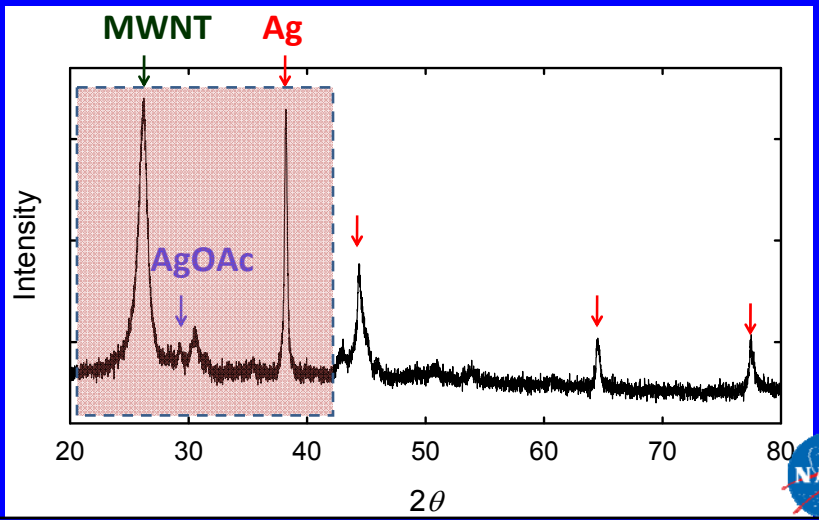
2-min Milling *without* Thermal Treatment



10-min Milling *without* Thermal Treatment

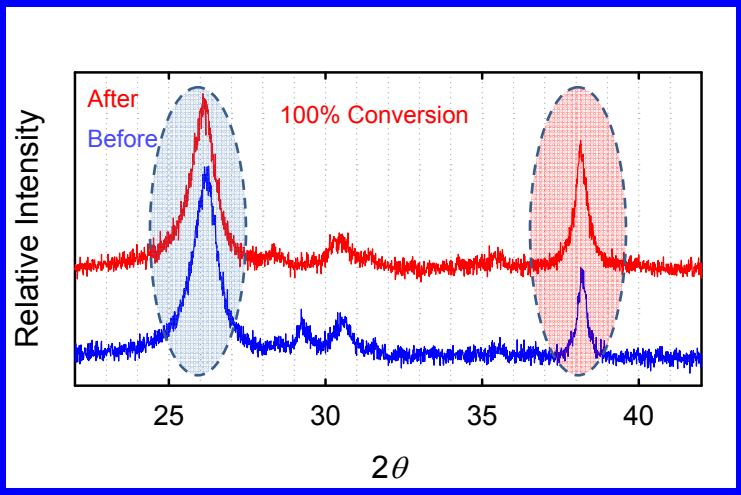


Formation of Ag (0) Nanoparticles on MWNT Surface



Estimated Yield of Conversion

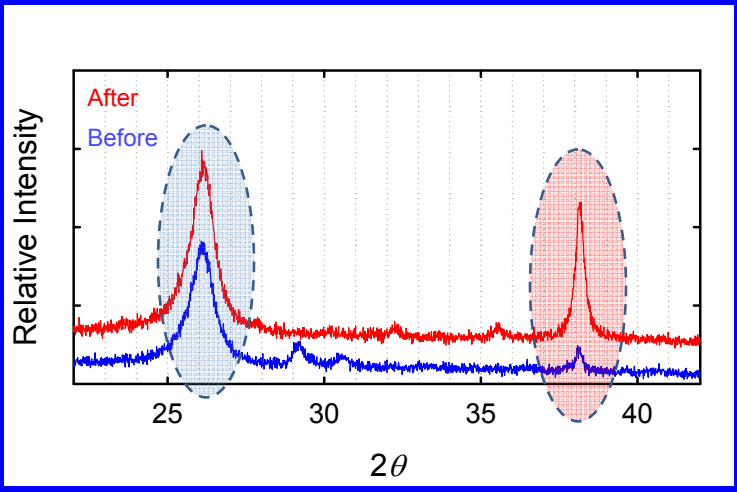
1 mol% AgOAc Feed (10-min Milling): ~40-60%



Estimation from Thermal Decomposition (350°C)

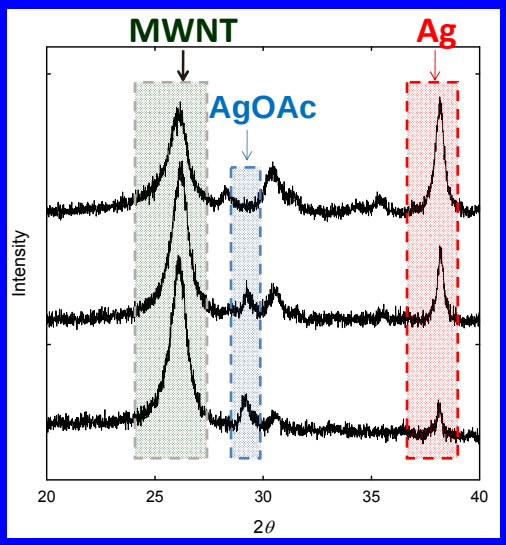
Shorter Milling, Less Conversion

1 mol% AgOAc Feed (2-min Milling): ~10-20%



Estimation from Thermal Decomposition

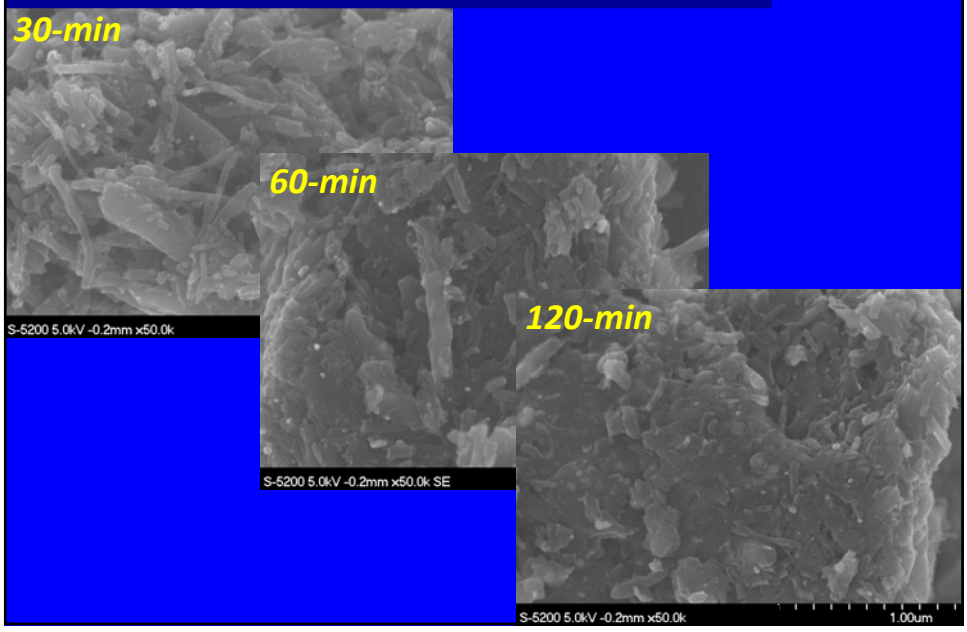
Conversion vs. Milling Time



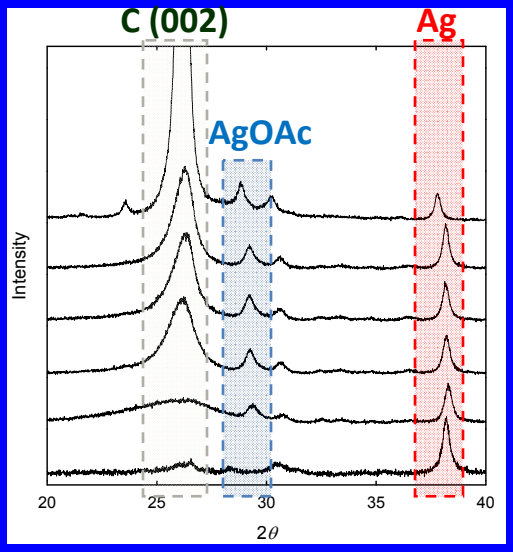
Ball-Mill Time	Yield
120-min	*>90%*
10-min	*40-60%*
2-min	*10-20%*

- 1% AgOAc Feed

Can't Mill Too Long



Dependence on CNT Diameter?



- *1% AgOAc Feed*
- *~10 min Milling*

CNT Diameter

Expanded Graphite

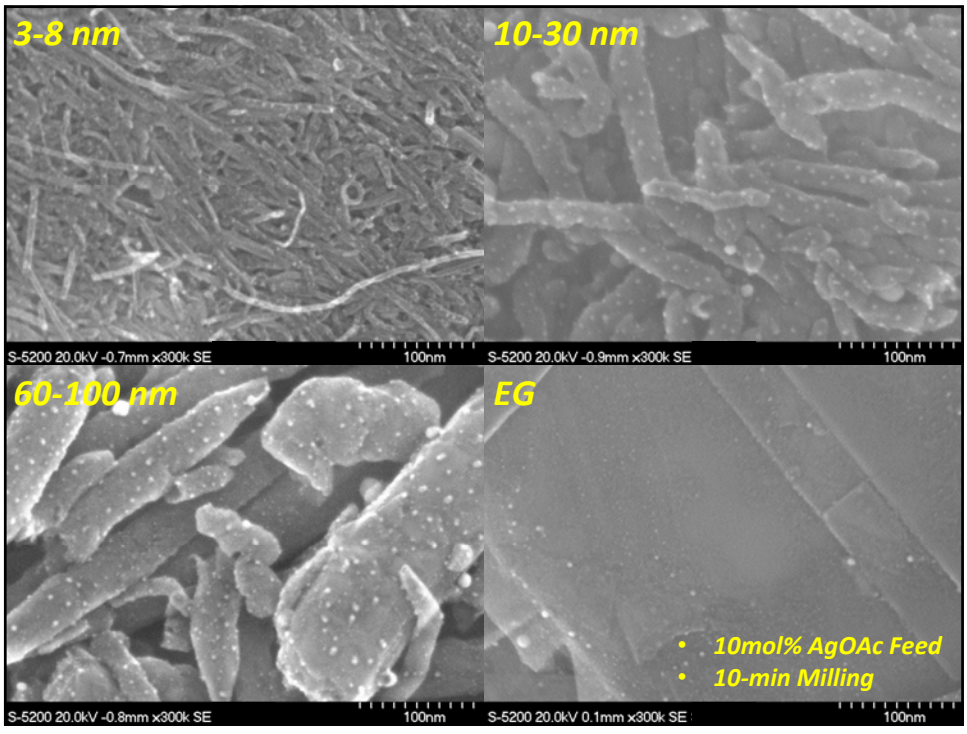
60-100 nm

40-60 nm

10-30 nm

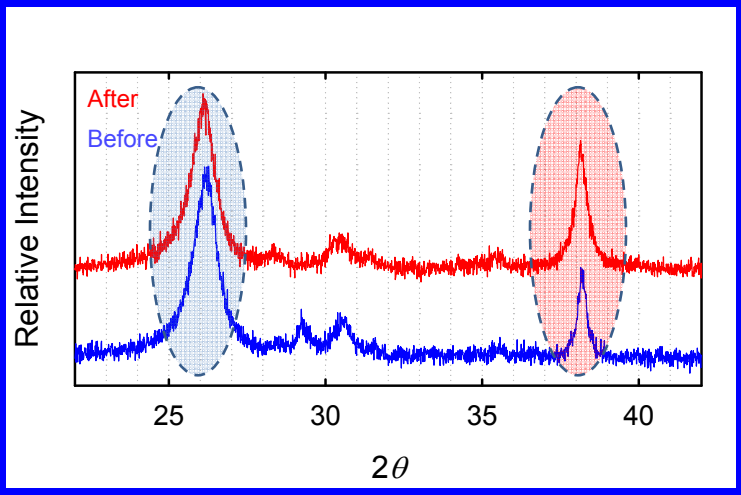
3-8 nm

SWNT



Yield of Conversion

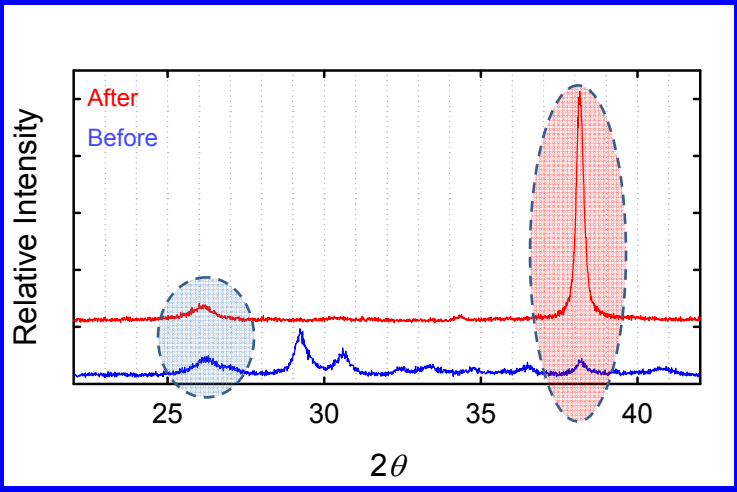
1 mol% AgOAc Feed (10-min Milling): ~40-60%



Estimation from Thermal Decomposition

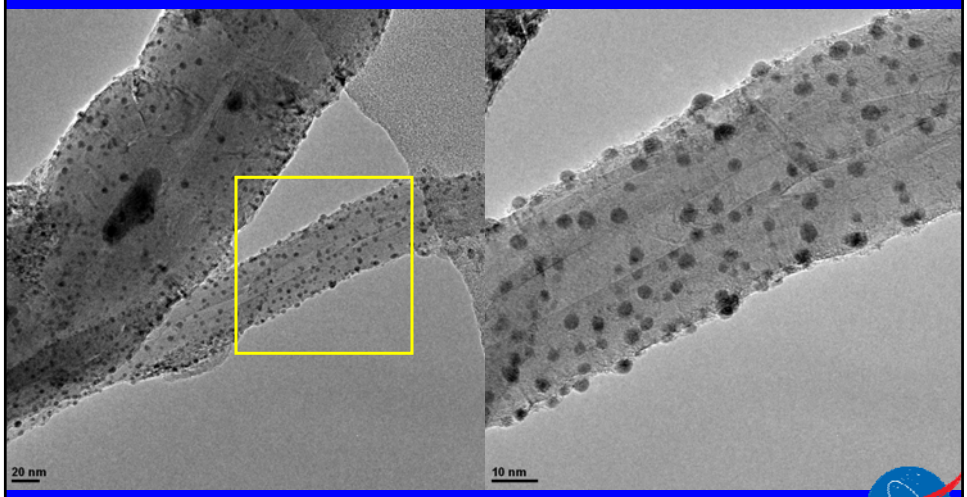
More Ag Feed, Less Conversion

10 mol% AgOAc Feed (10-min Milling): ~5-10%

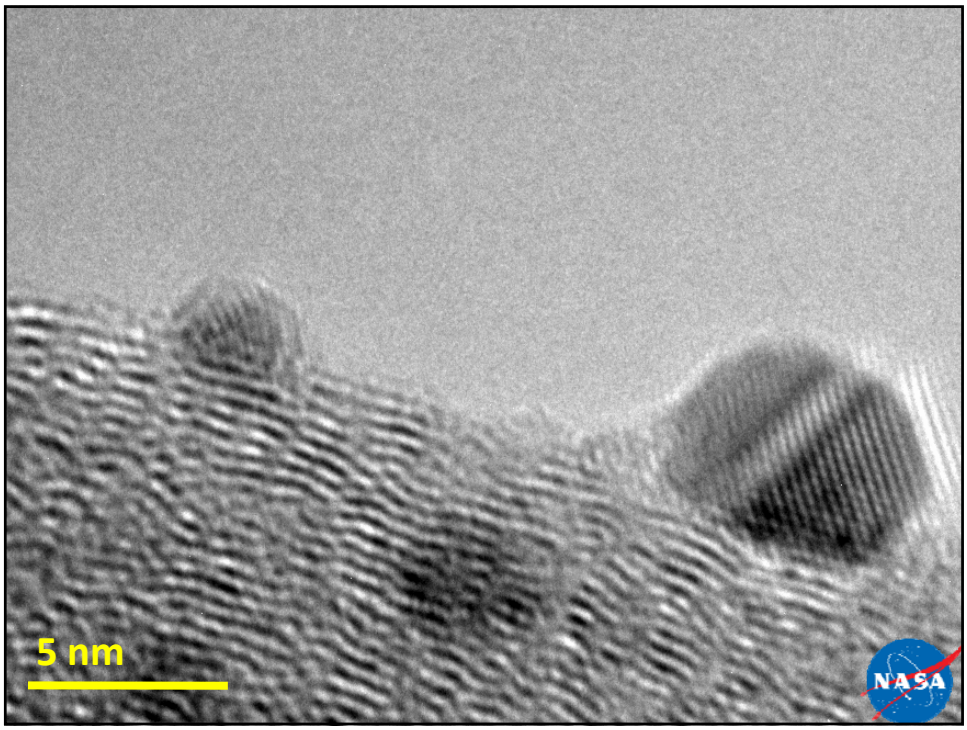


Estimation from Thermal Decomposition

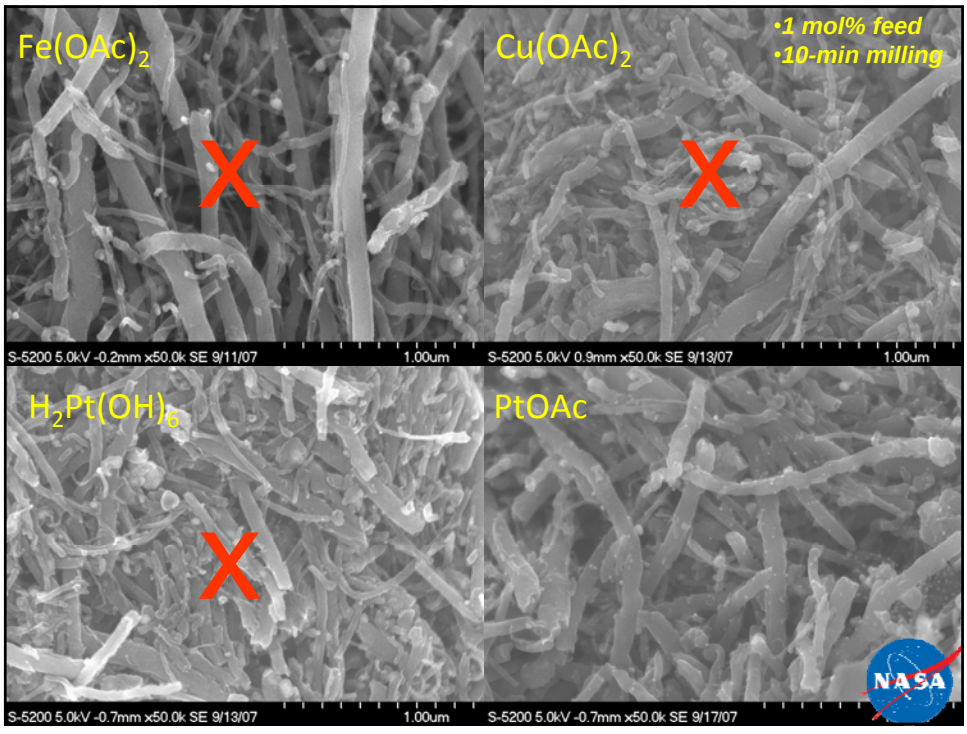
More Ag, More Decoration

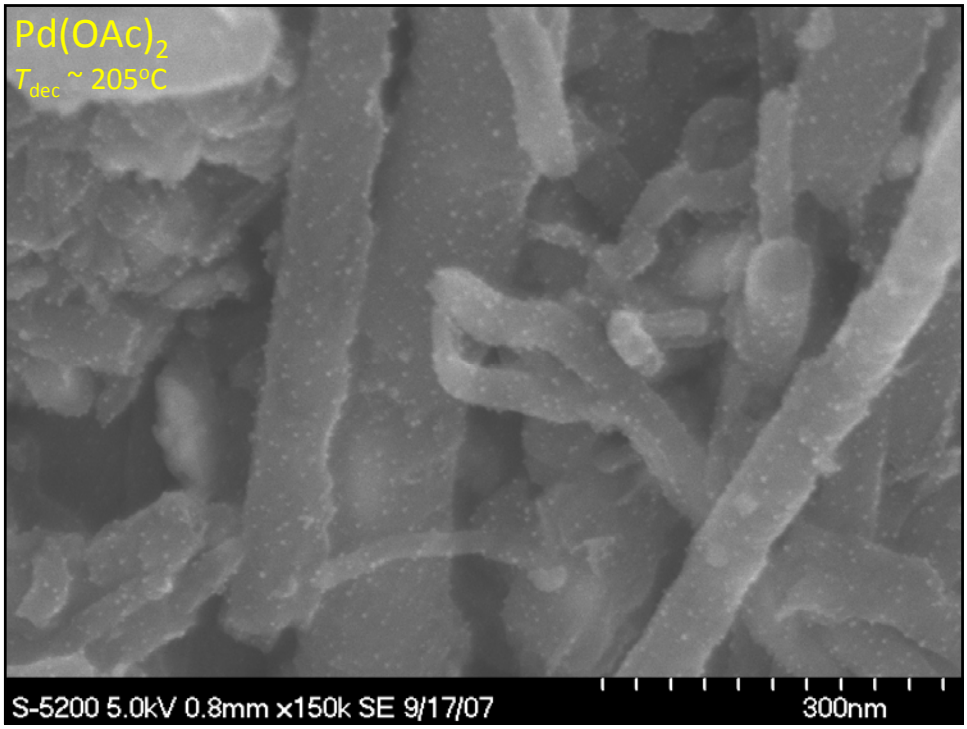


- *10 mol% AgOAc feed; 10-min milling*
- *Similar average size ~2.5 nm*

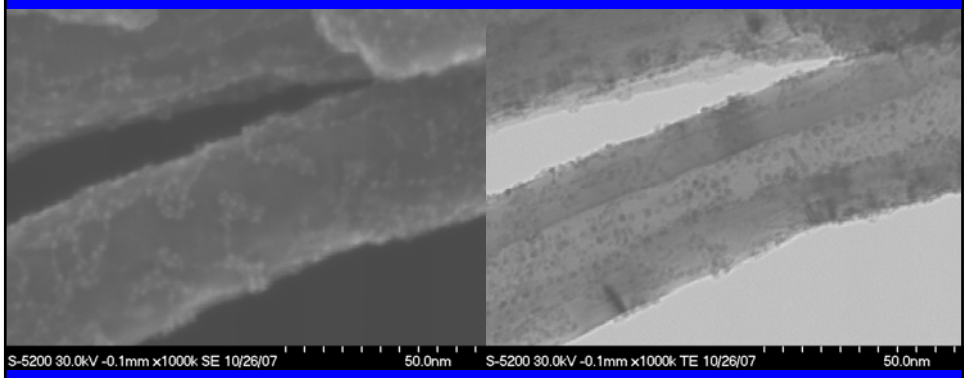


Other Metals?



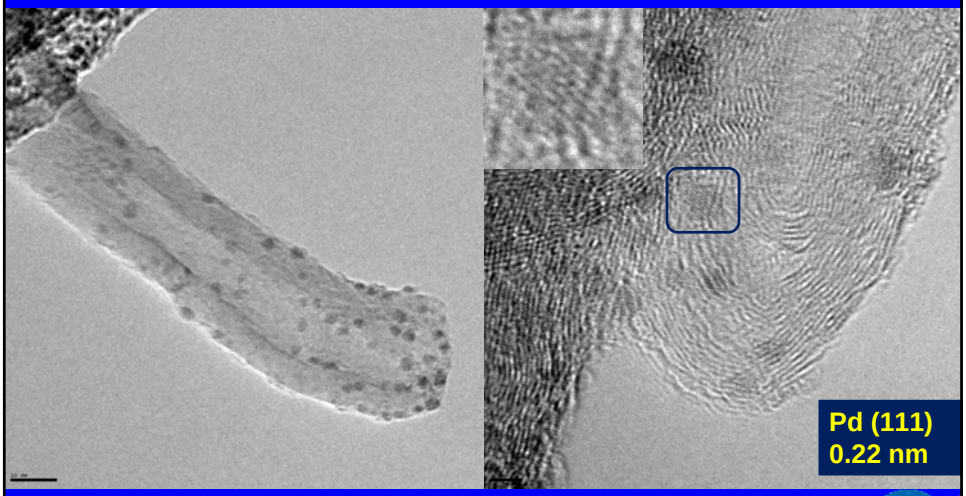


Pd Nanoparticle-Decorated MWNTs



- Homogeneous Decoration of sub-2nm Pd(0) nanoparticles
- Exhibit excellent catalytic properties

Pd Nanoparticle-Decorated MWNTs



Conclusions

- Advantages
  - Ambient conditions
  - Electroless, solventless, no reducing agent
  - Rapid, single-step (< 30 min), readily scaled up
  - Narrow size distribution (sub-5 nm)
  - Widely applicable to various carbon substrates
  - Applicable to various metals: Ag, Pd, Pt …
- Applications
  - Catalysis
  - Sensors
  - Electromagnetic devices
- Limitations
  - Corrosion at the expense of nanotube structural integrity
  - Not universal to all metal salts?

Acknowledgments

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  - NASA Postdoctoral Program managed by Oak Ridge Associated Universities (ORAU)
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  - Dr. Tony Belcher, Dr. Chris Wohl
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